SORPTION VELOCITY OF GAS BY POROUS SOLID.

By Jitsusaburo SAMESHIMA.

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A great number of papers are published on the sorption of gas by such porous solids as charcoal and silica gel, etc.[1] The author have also contributed papers on this subject.[2] There are, however, comparatively small number of investigations concerning the kinetics of sorption. The velocity of sorption is usually measured by the decrease of gas pressure existing in contact with solid matter. Thus the pressure of gas varies according to the sorption amount. Such mode of experiment is good for the determination of the vacuum producing power or the gas collecting power of charcoal, etc. It is better, however, to measure the sorption velocity under constant pressure for the study of mechanism of sorption.

Few papers are published which describe sorption velocity under constant pressure by porous solid. Giesen[3] measured the sorption of air, carbon dioxide and ammonia by box-wood charcoal, and Bergter[4] of air, nitrogen and oxygen by coconut charcoal.

Many data on the sorption velocity have already been published by the present author and his collaborators.[5] Above all, the sorption of ammonia by sugar charcoal was measured extending over six months.[6] From this experiment, the author obtained the following equation,

$$x - \alpha \log t = k \,,$$

where x denotes the quantity of gas sorbed at time t, α and k being constants. This equation was derived as follows.

By the author's opinion, the sorption of gas by porous solid is a process of entering gas molecules into the molecular cavities of solid

(1) Most of the important literatures on this subject are cited in the book: McBain, "The Sorption of Gases and Vapours by Solids" (1932).

(2) Sameshima and Hayashi, *Science Reports of the Tohoku Imperial University*, **12** (1924), 289; Sameshima and Watanabe, *J. Chem. Soc. Japan*, **47** (1926), 715; Sameshima, this Bulletin, **2** (1927), 1 and 246; **4** (1929), 96 and 125; *Chemical News*, **139** (1929), 61; this Bulletin, **5** (1930), 173 and 303; **6** (1931), 165; **7** (1932), 133.

(3) Giesen, *Ann. Physik*, **10** (1903), 838.

(4) Bergter, *Ann. Physik*, **37** (1912), 472.

(5) Sameshima, loc. cit.; Baba, this Bulletin, **5** (1930), 190.

(6) Sameshima, this Bulletin, **5** (1930), 173.

and forms a homogeneous solid solution.[1] The entering of gas molecules into comparatively large openings in solid is accomplished quickly. Then the gas molecules begin to enter into more narrow cavities among solid molecules overcoming a great resistance. Let us assume that the resistance encounters in entering into a narrow molecular cavity is proportional to the time required for it. Thus,

$$R = At$$

where R denotes the resistance, t the time and A a constant. Moreover, we obtain the following relation assuming the velocity of sorption is inversely proportional to the resistance,

$$\frac{dx}{dt} = \frac{B}{R},$$

where x is the quantity of gas sorbed, and B another constant. We have, therefore,

$$\frac{dx}{dt} = \frac{B}{At}.$$

Integrating this equation it becomes,

$$x = \frac{B}{A} \ln t + k$$

where k is the integration constant. Substituting another constant α we obtain,

$$x = \alpha \log t + k \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(I)}$$

see errata V. 7, P. 407

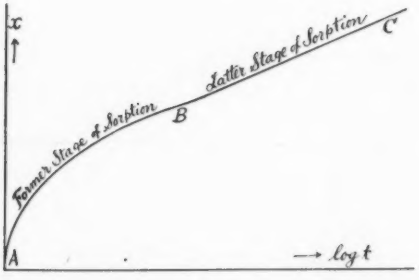

Fig. 1.

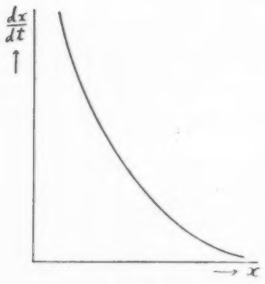

Fig. 2.

(1) Sameshima, this Bulletin, **4** (1929), 125; *Chem. News*, **139** (1929), 61.

Generally, the sorption velocity is expressed by a curve shown in Fig. 1, which has been drawn taking x against $\log t$. The curve converts into a straight line in the region of large t. Such a region, therefore, is expressed by Equation (I). The values of a and k can be evaluated by the slope and the height of intersection to x axis at $\log t = 0$. In the tables below, these values are given in the actual examples.

The former part of sorption, A to B in Fig. 1, cannot be expressed by Equation (I). This part corresponds to the entering of gas molecules into comparatively large openings in solid. The author proposes the following equation for this part,

$$\frac{dx}{dt} = K\frac{s-x}{x^n}$$

where s denotes the saturation amount, and K and n are constants. The value of s corresponds to the saturation value of the former part of sorption which amounts roughly to the height of B in Fig. 1. The exact value, however, cannot be obtained from the curve.

We assume, as usual, the velocity of sorption is proportional to the unoccupied space in solid, $(s-x)$. Moreover, the sorption proceeds by and by beginning with the place of greatest affinity between gas and solid. The places of great affinity will be occupied at first with great velocity, and the places of small affinity will be occupied slowly. In the later period, only the places of small affinity remains unoccupied by the gas molecule, so the sorption velocity becomes slower and slower in course of sorption. This behavior may be expressed by assuming that the velocity is inversely proportional to nth power of the occupied space x, thus $\frac{dx}{dt} \propto \frac{1}{x^n}$. The value of n is the measure of distribution of affinity between gas and solid.

We obtain, therefore, the following equation as already described.

$$\frac{dx}{dt} = K\frac{s-x}{x^n} \quad \cdots\cdots\cdots\cdots\cdots\cdots \text{(II)}$$

By integrating we have

$$-s^n \ln(s-x) + n s^{n-1}(s-x) - \frac{n(n-1)}{2} s^{n-2}\frac{(s-x)^2}{2} + \cdots\cdots$$

$$+ \frac{(-1)^{k-1} n!\, s^{n-k}}{(n-k)!\; k!}\frac{(s-x)^k}{k} + \cdots\cdots = Kt + \text{const.}$$

This is the general velocity equation for the former stage of sorption. The relation is expressed graphically as Fig. 2 plotting $\frac{dx}{dt}$ against x.

Now, taking the simplest case, we will assume $n=1$ in Equation (II), thus,

$$\frac{dx}{dt} = K\frac{s-x}{x} \quad \text{..... (III)}$$

By integration it becomes,

$$s-x-s\ln(s-x) = Kt+c,$$

where c denotes the integration constant. At $t=0$ the value of x is zero, so the integration constant is

$$c = s-s\ln s$$

Therefore, we have

$$s\ln\frac{s}{s-x}-x = Kt \quad \text{..... (IV)}$$

The former part of the curve in Fig. 1, from A to B, may be expressed by this equation.

Equation (IV) has been verified by experimental data. Good coincidence has been attained between calculated and observed data. Table 1 contains the data on the velocity of sorption of ammonia by sugar charcoal, the pressure of gas being 1 atmosphere and the temperature 25°C.[1] The first column indicates the time in minutes after the contact of ammonia to charcoal and the second the volume of gas sorbed by 0.3550 gr. recalculated to that at normal temperature and pressure. The third column of the table shows the value of K calculated by the equation

$$\frac{2.303\times 36.17}{t}\log\frac{36.17}{36.17-x}-\frac{x}{t} = K,$$

the fourth the value of k calculated by the equation,

$$x-1.032\log t = k,$$

the fifth the value of x calculated inversely from these equations taking $K=37.98$ and $k=35.10$ respectively, and the sixth the difference between observed (2nd column) and calculated (5th column) values of x.

(1) Sameshima, this Bulletin, **5** (1930), 173.

Table 1.

Sorption of Ammonia by Sugar Charcoal (25°C., 1 Atm.)

[Sameshima, this Bulletin, **5** (1930), 175.]

Time in min. t	Sorption amount in c.c. $x_{obs.}$	Velocity constants K	Velocity constants k	Sorption calculated $x_{calc.}$	Difference $x_{calc.}-x_{obs.}$
0.33	22.317	37.57		22.41	+ 0.09
0.77	24.345	20.90 ?		28.94	+ 4.60
1.27	32.29	38.16		32.30 (former stage)	+ 0.01
1.83	34.11	38.00		34.11 (former stage)	0
2.33	35.03	38.64		34.98 (former stage)	− 0.05
3.90	35.92	36.93		35.95 (former stage)	+ 0.03
10.83	36.483		—	—	—
21	36.776		35.412	36.465	− 0.311
67	37.183		35.299	36.985	− 0.198
140	37.382		35.167	37.315	− 0.067
306	37.692		35.127	37.665	− 0.027
1420	38.356		35.103	38.353	− 0.003
1660	38.401		35.078	38.423	+ 0.022
3065	38.675		35.077	38.698	+ 0.023
4425	38.837		35.074	38.863	+ 0.026
7280	39.049		35.063	39.086	+ 0.037
8740	39.138		35.070	39.168	+ 0.030
10160	39.218		35.083	39.235	+ 0.017
13140	39.305		35·054	39.351	+ 0.046
17310	39.423		35.049	39.474	+ 0.051
20140	39.515		35.073	39.542	+ 0.037
23270	39.589		35.083	39.606	+ 0.017
27450	39.668		35.087	39.681	+ 0.013
30225	39.726		35.102	39.724	− 0.002
37485	39.811		35.091	39.820	+ 0.009
41805	39.865		35.096	39.869	+ 0.004
50550	39.951		35.097	39.954	+ 0.003
57780	40.033		35.119	40.014	− 0.019
63360	40.077		35.122	40.055	− 0.022
73550	40.144		35.122	40.122	− 0.022
87885	40.234		35.132	40.202	− 0.032
103910	40.366		35.189	40.277	− 0.089
125290	40.440		35.179	40.361	− 0.079
149950	40.531		35.189	40.442	− 0.089
178760	40.577		35.157	40.520	− 0.057
208980	40.586		35.096	40.590	+ 0.004
229200	40.603		35.071	40.632	+ 0.029
279460	40.612		34.991	40.721	+ 0.109

Former stage : $$\frac{2.303\times 36.17}{37.98}\log\frac{36.17}{36.17-x}-\frac{x}{37.98}=t\,.$$

Latter stage : $$35.10+1.032\log t=x\,.$$

These results are depicted in Fig. 3 and Fig. 4. Fig. 3 shows the velocity of former stage of sorption and Fig. 4 that of latter stage of sorption. In Fig. 3 x is plotted against t while in Fig. 4 x against $\log t$. In these figures the observed data are shown by circlets and the calculated one by curves.

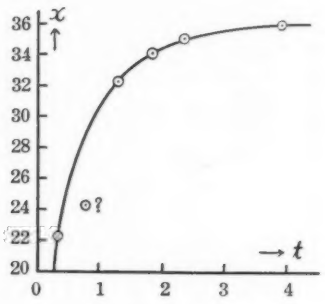

Fig. 3.

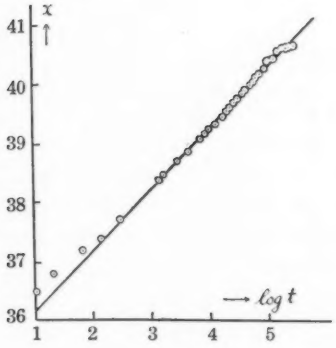

Fig. 4.

From Table 2 to Table 13 the results on various cases are given, in which, for the sake of brevity, only the values are given of time (t), the observed volume of gas sorbed (x_{obs}) and calculated value of x (x_{calc}). The calculations were done by the equations indicated under each table. The coincidence between observed and calculated values are generally good.

Table 2.

Sorption of Ammonia by Box-wood Charcoal (20°C., 488 mm.)

[Giesen, *Ann. Physik*, **10** (1903), 842.]

t	$x_{obs.}$	$x_{calc.}$	
1	28.	31.3	former stage
2	39.7	39.7	
3	45.7	44.7	
4	48.7	48.2	
5	50.7	50.5	
6	52.2	52.2	
7	52.9	53.5	
8	53.3	—	
9	53.6	—	
10	53.7	—	
15	54.3	54.4	
20	54.5	54.5	
30	54.7	54.6	
60	55.0	55.3	
120	55.1	55.1	
180	55.2	55.2	
240	55.2	55.2	

Former stage :

$$\frac{2.303 \times 58}{13.7} \log \frac{58}{58-x} - \frac{x}{13.7} = t .$$

Latter stage :

$$53.6 + 0.7 \log t = x .$$

Table 3.

Sorption of Carbon Dioxide by Box-wood Charcoal (18.5°C., 621 mm.)

[Giesen, *Ann. Physik*, **10** (1903), 842.]

t	$x_{obs.}$	$x_{calc.}$	
1	18.8	18.5	former stage
2	22.3	22.8	
3	25.2	25.1	
4	26.4	26.5	
5	27.3	27.3	
6	27.6	27.5	
7	27.7	27.7	
8	27.8	27.8	
9	27.9	27.9	
10	27.9	28.0	
15	28.3	28.5	
20	28.7	28.7	
30	29.3	29.2	
60	30.4	29.9	
120	30.8	30.6	
180	31.1	31.0	
240	31.2	31.3	
300	31.2	31.5	

Former stage :

$$\frac{2.303 \times 29.3}{10.56} \log \frac{29.3}{29.3-x} - \frac{x}{10.56} = t.$$

Latter stage :

$$25.7 + 2.35 \log t = x .$$

Table 4.

Sorption of Carbon Dioxide by Box-wood Charcoal (18.2°C., 496 mm.)

[Giesen, *Ann. Physik*, **10** (1903), 842.]

t	$x_{obs.}$	$x_{calc.}$	
1	16.0	16.2	former stage
2	20.4	20.2	
3	22.8	22.5	
4	23.9	24.0	
5	24.7	24.8	
6	25.2	25.2	
7	25.3	25.3	
8	25.4	25.4	
9	25.5	25.5	
10	25.6	25.6	
15	25.8	25.9	
20	26.0	26.0	
30	26.3	26.3	
60	26.8	26.8	
120	27.4	27.3	
180	27.6	27.6	
240	27.6	27.9	
300	27.6	27.9	

Former stage :

$$\frac{2.303 \times 27.0}{8.64} \log \frac{27.0}{27.0-x} - \frac{x}{8.64} = t.$$

Latter stage :

$$24.0+1.58 \log t = x .$$

Table 5.

Sorption of Air by Coconut Charcoal (18°C., 735.6 mm.)

[Bergter, *Ann. Physik*, **37** (1912), 482.]

t	$x_{obs.}$	$x_{calc.}$
0.75	16.31	—
1	17.15	—
2	18.45	18.47
3.67	19.27	19.14
5	19.56	19.48
7	19.87	19.85
9	20.09	20.06
10	20.23	20.25
13	20.49	20.54
15	20.62	20.70
20	20.93	21.02
25	21.17	21.27
30	21.47	21.47
40	21.78	21.78
50	22.01	22.03
60	22.28	22.23

Latter stage :

$$17.7+2.55 \log t = x .$$

Table 6.

Sorption of Ammonia by Silica Gel (25°C., 1 Atm.)

[Sameshima, this Bulletin, **7** (1932), 134.]

t	$x_{obs.}$	$x_{calc.}$	
0.5	29.00	28.84	former stage
1	35.14	35.23	
2	40.19	40.36	
5	43.29	43.19	
10	43.64	43.72	
20	43.96	43.94	
185	44.64	44.63	
1470	45.26	45.28	
7315	45.87	45.78	
17370	46.01	46.05	
33225	46.26	46.25	
77760	46.53	46.52	

Former stage :

$$\frac{2.303 \times 43.5}{37.0} \log \frac{43.5}{43.5-x} - \frac{x}{37.0} = t.$$

Latter stage :

$$43.0 + 0.72 \log t = x .$$

Table 7.

Sorption of Ammonia by Silica Gel (25°C., 1 Atm.)

[Sameshima, this Bulletin, **7** (1932), 134.]

t	$x_{obs.}$	$x_{calc.}$	
0.5	29.93	29.66	former stage
1.17	37.30	37.25	
2	41.11	40.93	
4	42.94	43.11	
6	43.20	43.20	
10	43.39	43.38	
15	43.52	43.51	
30	43.76	43.75	
50	43.96	43.92	
135	44.27	44.25	
280	44.48	44.50	
1585	45.02	45.08	
11520	45.85	45.75	

Former stage :

$$\frac{2.303 \times 43.5}{40.3} \log \frac{43.5}{43.5-x} - \frac{x}{40.3} = t.$$

Latter stage :

$$42.6 + 0.775 \log t = x .$$

Table 8.

Sorption of Carbon Dioxide by Silica Gel (25°C., 1 Atm.)

[Sameshima, this Bulletin, **7** (1932), 135.]

t	$x_{obs.}$	$x_{calc.}$	
0.5	4.66	4.65	former stage
1	5.03	5.17	
2	5.38	5.38	
5	5·56	5.60	
10	5·66	5.66	
60	5.82	5.81	
255	5.93	5.93	
1380	6.08	6.07	
2995	6.16	6.13	
11490	6.27	6.24	
34550	6.34	6.34	
82050	6.40	6.40	

Former stage:

$$\frac{2.303\times 5.4}{12.0}\log\frac{5.4}{5.4-x}-\frac{x}{12.0}=t.$$

Latter stage:

$$5.47+0.19\log t=x.$$

Table 9.

Sorption of Ammonia by Opal (25°C., 1 Atm.)

[Sameshima, this Bulletin, **6** (1931), 168.]

t	$x_{obs.}$	$x_{calc.}$
0.5	2.52	—
2	3.07	2.93
10	3.71	3.68
30	4.20	4.20
60	4.52	4.52
120	4.84	4.84
240	5.17	5.17
1460	5.99	6.02
4320	6.55	6.52

$$2.60+1.08\log t=x.$$

Table 10.

Sorption of Ammonia by Diatomaceous Earth (25°C., 1 Atm.)

[Sameshima, this Bulletin, **6** (1931), 165.]

t	$x_{obs.}$	$x_{calc.}$
0.5	11.69	—
2	14.20	14.87
5	15.46	15.43
10	15.92	15.86
30	16.61	16.54
60	16.97	16.97
120	17.33	17.39
240	17.67	17.82
1560	18.86	18.97
4330	19.57	19.60
7370	19,93	19.93
11635	20.21	20.21
18850	20.47	20.51

$$14.44+1.42\log t = x\,.$$

Table 11.

Sorption of Ammonia by Chabazite (25°C., 1 Atm.)

[Sameshima, this Bulletin, **4** (1929), 101.]

t	$x_{obs.}$	$x_{calc.}$	
0.3	115.6	119.0	former stage
1	149.1	148.5	
2.5	181.7	181.9	
5	194.9	194.9	
10	197.2	197.1	latter stage
30	198.4	198.0	
68	198.5	198.6	
270	199.9	199.6	
1430	200.4	200.8	

Former stage:

$$\frac{2.303\times 198}{126}\log\frac{198}{198-x}-\frac{x}{126}=t\,.$$

Latter stage:

$$195.4+1.73\log t = x\,.$$

Table 12.

Sorption of Carbon Dioxide by Chabazite (25°C., 768.9 mm.)

[Baba, this Bulletin, **5** (1930), 194.]

t	$x_{obs.}$	$x_{calc.}$
0.42	23.3	—
1	36.8	—
1.5	41.6	42.0
2	44.1	43.5
3	45.9	45.5
5	47.8	48.0
10	51.0	51.5
20	54.3	55.0
42	59.1	58.7
60	60.9	60.5
120	64.2	63.9

$$40.0+11.5\log t = x\,.$$

Table 13.

Sorption of Carbon Dioxide by Chabazite (25°C., 772 mm.)

[Baba, this Bulletin, **5** (1930), 195.]

t	$x_{obs.}$	$x_{calc.}$
0.45	38.6	—
2	70.4	—
3	75.1	75.5
5	77.6	77.5
10	80.2	80.0
20	82.4	82.6
45	85.3	85.5
80	87.8	87.7
120	89.3	89.2
180	90.8	90.7
1200	96.2	97.7

$$71.5+8.5\log t = x\,.$$

Summary.

1. The sorption by porous solid of gas under constant pressure and temperature proceeds, generally, in two stages. The mechanisms of sorption of each stage are described.

2. The velocity of the former stage is expressed by the equation

$$\frac{dx}{dt} = K\frac{s-x}{x^n}$$

where x denotes the amount of gas sorbed at time t, and K, s and n are constants. In the simplest case where $n=1$, this equation is integrated in the following form,

$$\frac{s}{t}\ln\frac{s}{s-x} - \frac{x}{t} = K.$$

3. The velocity of the latter stage of sorption is expressed by

$$x - a\log t = k$$

where a and k are constants.

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POTENTIOMETRIC TITRATION OF SODIUM AND POTASSIUM FERROCYANIDE.

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On the potentiometric titration of potassium and sodium ferrocyanide with metallic salts were already reported by many investigators. In 1915, Knauth[1] was studied on the potentiometric titration of potassium ferrocyanide with zinc salt by using zinc electrode as the indicator electrode and he showed that the titration might be made by the potentio-

(1) *Dissert. Dresden* (1915).

metric method. This was confirmed quite independently by Bischowsky,[1] and G. Hedrich[2] concluded that the method gave highly accurate results by the special study of this titration and also Kolthoff and Verzijl[3] was done a special study of the absolute accuracy of the method. Treadwell and Chervet[4] stated that the composition of a metal ferrocyanide depends upon the alkali metal of the ferrocyanide and they found that in titrating zinc with potassium ferrocyanide the composition of ferrocyanide was $K_2Zn_3[Fe(CN)_6]_2$, while with sodium ferrocyanide $Zn_2Fe(CN)_6$.

Hedrich also stated that the break in potential does not occur exactly at the point corresponding to the formation of $K_2CdFe(CN)_6$ in the titration of a cadmium salt with potassium ferrocyanide. Müller and Gabler[5] investigated the titration of lead with ferrocyanide and also they obtained good results when the lead concentration is larger than 0.01 molal. Hedrich studied the titration of potassium ferrocyanide with cupric salt and Niemz[6] with silver salt at 70°C. But Müller showed that the ferrocyanide titration is not suitable for the determination of silver and copper.

In this investigation the potentiometric titration of potassium and sodium ferrocyanide with mercuric chloride, nickel sulphate and cobalt sulphate by using platinum electrode as the indicator electrode at 25°C. were employed.

In the titration of potassium and sodium ferrocyanide with metallic salts, the reactions take place as follows.

$$2Hg^{++} + Fe(CN)_6^{----} = Hg_2Fe(CN)_6 \qquad (1)$$

$$2Ni^{++} + Fe(CN)_6^{----} = Ni_2Fe(CN)_6 \qquad (2)$$

$$2Co^{++} + Fe(CN)_6^{----} = Co_2Fe(CN)_6 \qquad (3)$$

In the above reactions the potential is governed by the following equation by adding a little ferricyanide to the solution and taking bright platinum as the indicator electrode.

$$E = e + 0.0591 \log \frac{[Fe(CN)_6^{---}]}{[Fe(CN)_6^{----}]} \qquad (4)$$

(1) *J. Ind. Eng. Chem.*, **9** (1917), 668.
(2) *Dissert. Dresden* (1915).
(3) *Rec. Trav. Chim.*, **43** (1924), 380; *Z. anorg. Chem.*, **132** (1923), 318.
(4) *Helv. Chim. Acta.*, **5** (1922), 633.
(5) *Z. analyt. Chem.*, **62** (1923), 29.
(6) *Dissert. Dresden* (1920).

From the reactions (1), (2) and (3), we have next equation,

$$[Fe(CN)_6^{----}] = \frac{S_{Me_2Fe(CN)_6}}{[Me^{++}]^2}$$

By substituting this value in equation (4) and taking $[Fe(CN)_6^{----}]$ as a constant, we have

$$E_{Fe(CN)_6} = e' - 0.0591 \times 2P_{Me}$$

Therefore we knew that the ferrocyanide electrode responds to the concentration of metal ions (Ni^{++}, Co^{++}, Hg^{++}).

Experimental Part.

Potassium and sodium ferrocyanide, potassium and sodium ferricyanide, mercuric chloride, nickel suphate and cobaltous sulphate used were of Kahlbaum's. These salts were purified by recrystallization. One-tenth molal solutions of these salts were prepared very carefully.

(1) Titration by Sodium Ferrocyanide with Mercuric Chloride. 10 C.c. of one-tenth molal solution of sodium ferrocyanide and 1 c.c. of one-tenth molal sodium ferricyanide were taken in the half cell and this solution diluted to 100 c.c. with conductance water, and then the half cell was connected with decinormal calomel electrode with decinormal salt bridge. After the cell was kept in a thermostat at 25±0.05°C. for one hour, the electromotive forces of the cell were measured. Then a c.c. of mercuric chloride solution was added from the burette into the half cell and stirred, and then the electromotive force of the cell was measured. The results are summarized in Table 1.

In the above titration, when 5 c.c. of mercuric chloride solution were added to sodium ferrocyanide solution, the solution took green colour. As it can be seen in Table 1 and Fig. 1, we obtained 20.05 c.c. as the end point.

(2) Titration by Mercuric Chloride with Sodium Ferrocyanide. 40 C.c. of one-tenth molal solution of mercuric chloride was taken and this solution was diluted to 100 c.c. with conductivity water, and then the titration was done by the one-tenth molal solution of sodium ferrocyanide. The results are summarized in Table 2.

In Table 2 and Fig. 1, we obtained 20.02 c.c. as the maximum point. During the titration, the solution changed yellow to blueish green. We had very good agreement with each other.

Table 1.

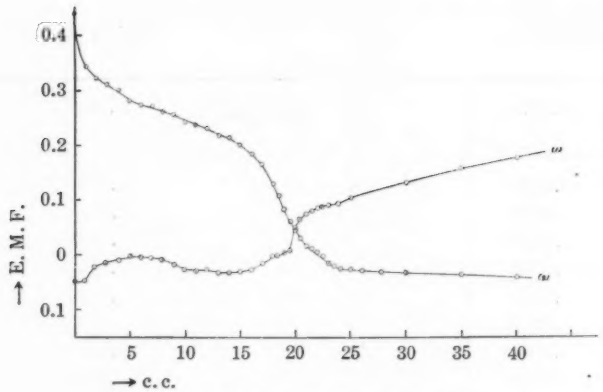
C.c. of $HgCl_2$ a	E. M. F. b	$\frac{\Delta b}{\Delta a}$
0	−0.04616	
		1150
2	.02316	
		997
3	.01319	
		519
4	.00800	
		172
5†	.00628	
		158
6	.00470	
		162
7	.00632	
		104
8	.00736	
		917
9	.01653	
		939
10	.02592	
		333
11	.02925	
		185
12	.02740	
		744
13	.03484	
		484
14	.03000	
		150
15	.02850	
		225
16	.02625	
		1000
17	.01625	
		763
18	.00862	
		1535
19	+.00125	
		3699
20	.04920	
		3918*
20.5	.06605	
		1850
21	.07530	
		1020
21.5	.08040	
		860
22	.08470	
		610
22.5	.08775	
		450
23	.09000	
		384
24	.09384	
		316
25	.09700	
		808
30	.13742	
		400
35	.15742	
		250
38	.16745	
		327
40	.17400	

† Green colour.
* Maximum point.
Experimental value 20.05 c.c.

Table 2.

C.c. of $Na_4Fe(CN)_6$ a	E. M. F. b	$\frac{\Delta b}{\Delta a}$
0	0.43690	
		9645
1	.34045	
		2045
2	.32000	
		1150
3	.30850	
		850
4	.30000	
		800
5	.29200	
		680
6	.28520	
		425
7	.28095	
		829
8	.27266	
		726
9	.26540	
		1394
10	.25146	
		497
11	.24649	
		729
12	.23920	
		955
13	.22965	
		1190
14	.21775	
		1425
15	.20350	
		1990
16	.18360	
		2000
17	.16360	
		2730
18	.13630	
		3660
18.5	.11800	
		4470
19	.09395	
		4690
19.5	.07050	
		4732
20	.04574	
		5038*
20.5	.02055	
		1250
21	.01430	
		954
21.5	.00953	
		808
22	.00549	
		549
23	.00000	
		1520
24	−.01520	
		345
25	.01865	
		541
26	.02406	
		228
30	.03320	
		69
35	.03665	
		41
40	.03870	

* Maximum point.
Experimental value 20.02 c.c.



(1) with mercuric chloride titrated
(2) with $Na_4Fe(CN)_6$ titrated

Fig. 1.

(3) Titration by Nickel Sulphate with Potassium Ferrocyanide. 20 C.c. of one-tenth molal solution of nickel sulphate was taken in the half cell and diluted to 100 c.c. with conductivity water and then titrated with 0.1 molal solution of potassium ferrocyanide after the cell was kept in a thermostat at 25±0.05°C. for one hour. The results are summarized in Table 3. In this case we obtained 10.06 c.c. at the maximum point. The ratio of Ni to ferrocyanide is 1.98:1.

(4) Titration by Potassium Ferrocyanide with Nickel Sulphate. 5 C.c. of one-tenth molal potassium ferrocyanide solution and 0.5 c.c. of one-tenth molal solution of potassium ferricyanide were taken in the half cell and the solution diluted to 100 c.c. and then this solution titrated with nickel sulphate solution. The results are shown in Table 4. As it can be seen in the Table 4 and Fig. 2, we obtained 9.95 c.c. as the maximum point. This value is very good agreement with other.

(5) Titration by Potassium Ferrocyanide with Cobaltous Sulphate. 5 C.c. of one-tenth molal solution of potassium ferrocyanide and 0.5 c.c. of one-tenth molal solution of potassium ferricyanide were taken and the mixed solution was diluted to 100 c.c. with conductivity water, and then titrated with one-tenth molal solution of cobaltous sulphate. The results are summarized in Table 5. As it can be seen in the Table 5 and Fig. 3, we obtained 10.02 as the maximum point. Therefore the ratio of Co to ferrocyanide is 1: 2.004.

Table 3.

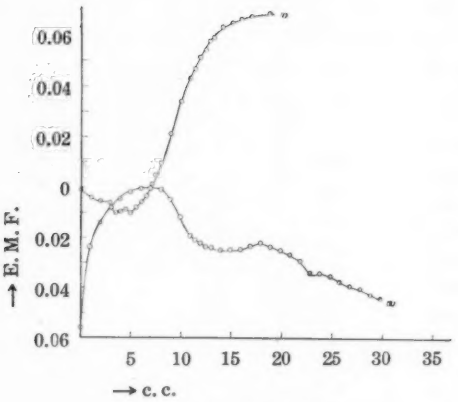
C.c. of $K_4Fe(CN)_6$ a	E. M. F. b	$\frac{\Delta b}{\Delta a}$
0	−0.05585	
		3190
1	.02395	
		1009
2	.01386	
		706
3	.00680	
		182
4	.00498	
		300
5	.00198	
		136
6	.00062	
		37
7	.00025	
		—
8	.00025	
		255
8.5	.00280	
		368
9	.00464	
		600
9.5	.00764	
		800
10	.01164	
		884*
10.5	.01606	
		700
11	.01956	
		344
11.5	.02128	
		268
12	.02262	
		·45
13	.02307	
		93
14	.02400	
		50
15	.02450	
		125
16	.02420	
		100
17	.02320	
		32
18	.02288	
		179
19	.02467	
		80
20	.02547	
		222
21	.02767	
		200
22	.02967	
		513
23	.03480	
		—
24	.03480	
		100
25	.03580	
		315
26	.03895	
		177
27	.04072	
		200
28	.04272	
		106
29	.04378	
		99
30	.04477	

* Maximum point.
Experimental value 10.06 c.c.

Table 4.

C.c. of $NiSO_4$ a	E. M. F. b	$\frac{\Delta b}{\Delta a}$
0	−0.000225	
		3375
1	.003600	
		2220
2	.005820	
		285
3	.005535	
		8310
3.5	.009690	
		2000
4	.008690	
		360
4.5	.008370	
		1368
5	.009554	
		4278
5.5	.007415	
		4652
6	.005089	
		2178
6.5	.004000	
		8000
7	.000000	
		9000
7.5	+0.004500	
		9000
8	.009000	
		10000
8.5	.014000	
		11100
9	.019550	
		11150
9.5	.025125	
		13750*
10	.032000	
		13020
10.5	.038510	
		10980
11	.044000	
		6000
11.5	.047000	
		8000
12	.051000	
		6000
13	.057000	
		6111
14	.063111	
		2689
15	.065800	
		—
16	.065800	
		2000
17	.067800	
		3800
18	.068184	
		1331
19	.069525	
		—
20	.069525	

* Maximum point.
Experimental value 9.95 c.c.



(1) with $NiSO_4$ titrated
(2) with $K_4Fe(CN)_6$ titrated

Fig. 2.

(6) Titration by Cobaltous Sulphate with Potassium Ferrocyanide. 20 C.c. of one-tenth molal cobaltous sulphate solution were taken and diluted to 100 c.c. with conductance water and then titrated one-tenth molal potassium ferrocyanide at 25±0.05°C. We obtained the results shown in Table 6. We obtained 9.98 c.c. as the maximum point from the Table 6 and Fig. 3. Hence we knew that the ratio of Co to ferrocyanide is corresponding to 1 : 1.996.

(7) Titration by Potassium and Sodium Ferrocyanide with Ferric Chloride and Silver Nitrate. As already mentioned above, we studied the potentiometric titration by potassium and sodium ferrocyanide with metallic salts. In the following experiments, the potentiometric titration compared with potassium and sodium ferrocyanide by the solutions of ferric chloride and silver nitrate at the same condition or different condition.

Ferric chloride and silver nitrate used were of Kahlbaum's. These salts were purified by washing with conductance water and then each 0.1 molal solution was prepared very carefully.

At first the potentiometric titration was carried out with 0.1 molal solution of potassium and sodium ferrocyanide by 0.1 molal solution of ferric chloride and at the second by 0.1 molal solution of silver nitrate. Each 10 c.c. of 0.1 molal solution of potassium and sodium

Table 5.

C.c. of $CoSO_4$ a	E. M. F. b	$\frac{\Delta b}{\Delta a}$
0	−0.00108	
		49
1	.00157	
		27
2	.00185	
		185
3	.00000	
		—
4	.00000	
		102
5	+0.00102	
		274
6	.00376	
		124
7	.00500	
		300
8	.00800	
		200
8.5	.00900	
		210
9	.01010	
		380
9.5	.01200	
		390
10	.01395	
		510*
10.5	.01750	
		300
11	.01900	
		200
11.5	.02000	
		150
12	.02150	
		120
13	.02270	
		243
14	.02513	
		282
15	.02795	
		165
16	.02950	
		304
17	.03254	
		200
18	.03454	
		117
19	.03571	
		168
20	.03739	
		201
25	.03940	
		60
30	.04000	

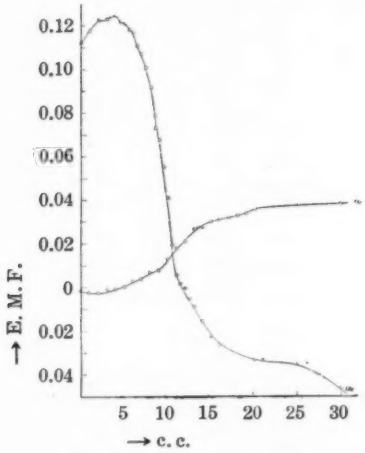
* Maximum point.
Experimental value 10.02 c.c.

Table 6.

C.c. of $K_4Fe(CN)_6$ a	E. M. F. b	$\frac{\Delta b}{\Delta a}$
0	0.11565	
		535
1	0.12100	
		560
2	0.12660	
		—
3	.12660	
		130
3.5	.12790	
		—
4	.12790	
		550
4.5	.12515	
		180
5	.12425	
		540
5.5	.12155	
		310
6	.12000	
		1280
6.5	.11360	
		580
7	.11070	
		1410
7.5	.10365	
		1900
8	.09415	
		2850
8.5	.08090	
		2180
9	.07000	
		2590
9.5	.05705	
		4902*
10	.03254	
		2508
10.5	.02000	
		2800
11	.00600	
		800
11.5	.00200	
		400
12	.00000	
		1000
12.5	−0.00500	
		800
13	.00900	
		700
14	.01600	
		750
15	.02350	
		430
16	.02780	
		163
20	.03434	
		53
25	.03550	
		253
30	.04765	

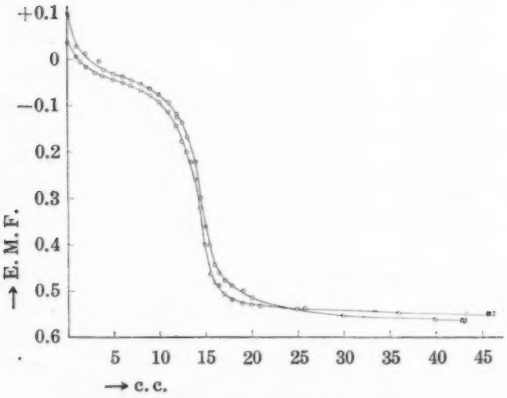
* Maximum point.
Experimental value 9.98 c.c.

ferrocyanide and 1 c.c. of 0.1 molal solution of potassium and sodium ferricyanide were taken and these solutions diluted to 100 c.c. with conductance water and then each solution was titrated by 0.1 molal solution of ferric chloride. The platinum electrode was used as the indicator electrode. The results are summarized as Tables 7 and 8.



(1) with $CoSO_4$ titrated
(2) with $K_4Fe(CN)_6$ titrated

Fig. 3.



(1) with $Na_4Fe(CN)_6$ titrated
(2) with $K_3Fe(CN)_6$ titrated

Fig. 4.

Table 7.

Titration by $K_4Fe(CN)_6$ with Ferric Chloride

C.c. of $FeCl_3$ a	E. M. F. b	$\frac{\Delta b}{\Delta a}$
0	0.04566	
		3460
1	.01106	
		31
2	−0.01075	
		1274
3	.02349	
		783
4	.03132	
		694
5	.03826	
		714
6	.04540	
		866
7	.05406	
		818
8	.06224	
		1096
9	.07320	
		1560
10	.08880	
		1906
11	.10786	
		3486
12	.14272	
		3286
12.5	.17555	
		4070
13	.19590	
		4564
13.5	.21872	
		7816
14	.25780	
		12004
14.5	.31782	
		16000*
15	.39782	
		13216
15.5	.46390	
		3220
16	.48000	
		1900
16.5	.48950	
		3644
17	.50772	
		1038
18	.51810	
		850
19	.52660	
		175
21	.53010	
		261
26	.54132	
		69
36	.54825	
		27
46	.55000	

* Maximum point
Experimental value 14.62 c.c.

Table 8.

Titration by $Na_4Fe(CN)_6$ with Ferric Chloride

C.c. of $FeCl_3$ a	E. M. F. b	$\frac{\Delta b}{\Delta a}$
0	0.10500	
		6977
1	.03523	
		1736
2	.01787	
		1577
3	.00210	
		1985
4	−0.01775	
		896
5	.02671	
		659
6	.03330	
		670
7	.04000	
		972
8	.04972	
		973
9	.05945	
		1435
10	.07380	
		1620
11	.09000	
		2570
12	.11570	
		3450
12.5	.13295	
		6520
13	.16555	
		5474
13.5	.19292	
		5196
14	.21890	
		16000*
14.5	.29890	
		12302
15	.36041	
		8658
15.5	.40370	
		8000
16	.44370	
		4600
16.5	.46670	
		2340
17	.47840	
		1610
18	.48645	
		1355
19	.50000	
		1514
20	.51514	
		1266
21	.52780	
		412
25	.54450	
		200
30	.55450	
		111
40	.56566	

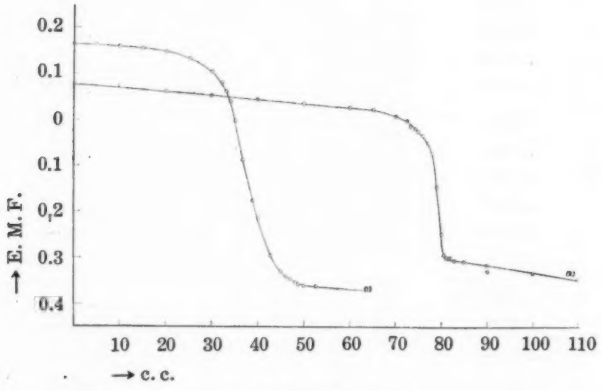
* Maximum point
Experimental value 14.60 c.c.

As it was shown in Tables 7 and 8 and Fig. 4, the electromotive force in the case of sodium ferrocyanide was very little greater than that of potassium ferrocyanide before 25 c.c. of ferric chloride solution were added to potassium and sodium ferroyanide solution, but after 25 c.c. of ferric chloride solution were added to each solution, the former electromotive force was a little lower. However the maximum value of each case was nearly same. That is, the value for sodium ferrocyanide was 14.60 c.c. and for potassium ferrocyanide 14.62 c.c. Therefore each reaction will take place as follows.

$$3Na_4Fe(CN)_6+4FeCl_3 = Fe_4[Fe(CN)_6]_3+12NaCl$$

$$3K_4Fe(CN)_6+4FeCl_3 = Fe_4[Fe(CN)_6]_3+12KCl$$

The following potentiometric titrations were carried out by the different conditions. That is, 20 c.c. of 0.1 molal solution of sodium ferrocyanide and 10 c.c. of 0.1 molal solution of potassium ferrocyanide were taken and then 1 c.c. of 0.1 molal solution of sodium ferricyanide and potassium ferricyanide were added to each solution. These solutions were titrated with 0.1 molal solution of silver nitrate. The results are summarized in Tables 9 and 10. As it is shown in Fig. 5, each curve was of the same type and we obtained 39.35 c.c. and 78.80 c.c. at the above titration. Therefore the difference of c.c. at the maximum



(1) with $K_4Fe(CN)_6$ titrated
(2) with $Na_4Fe(CN)_6$ titrated

Fig. 5.

Table 9.

Titration by $Na_4Fe(CN)_6$ with Silver Nitrate

C.c. of $AgNO_3$ a	E. M. F. b	$\frac{\Delta b}{\Delta a}$
0	0.07441	
		4
10	.07397	
		147
20	.05925	
		82
30	.05104	
		10
40	.04000	
		47
50	.03525	
		78
60	.02740	
		133
65	.02074	
		214
70	.01000	
		500
72	.00000	
		1580
73	−0.01580	
		698
74	.02278	
		367
75	.02645	
		1020
76	.03665	
		1171
77	.04836	
		1039
77.5	.05875	
		2770
78	.07260	
		6774
78.5	.10647	
		10878*
79	.16086	
		9698
79.5	.20935	
		8000
80	.24935	
		7890
80.5	.28880	
		2280
81	.30020	
		198
81.5	.30119	
		—
82	.30119	
		475
83	.30594	
		—
84	.30594	
		—
85	.30594	
		210
90	.31745	
		170
100	.33445	
		131
110	.34760	

* Maximum point
Experimental value 78.80 c.c.

Table 10.

Titration by $K_4Fe(CN)_6$ with Silver Nitrate

C.c. of $AgNO_3$ a	E. M. F. b	$\frac{\Delta b}{\Delta a}$
0	0.16385	
		90
5	.15934	
		80
10	.15530	
		53
15	.15265	
		78
20	.14875	
		450
25	.12846	
		465
30	.10520	
		1090
32	.08340	
		2128
33	.06212	
		3132
34	.03080	
		3080
35	.00000	
		3730
36	−0.03730	
		5045
37	.08775	
		5191
38	.13966	
		5468
38.5	.16700	
		5632
39	.19516	
		6778*
39.5	.22905	
		4000
40	.24905	
		2164
43	.31399	
		1147
45	.33694	
		901
46	.34595	
		215
47	.34810	
		760
48	.35655	
		789
49	.36444	
		—
50	.36444	

* Maximum point
Experimental value 39.35 c.c.

point was 0.1 c.c. and also the ratio of silver to ferrocyanide is corresponding to 1 : 3.935 or 1 : 3.940. Hence we knew that the reaction takes place in each case as follows.

$$4Ag^{+} + Fe(CN)_6^{----} = Ag_4Fe(CN)_6$$

Summary.

(1) The potentiometric titrations of potassium and sodium ferrocyanide with mercuric chloride, nickel sulphate and cobaltous sulphate by using platinum electrode as an indicator electrode were studied at 25°C.

(2) From the above titration we found that the reactions take place as follows.

$$2Hg^{++} + Fe(CN)_6^{----} = Hg_2Fe(CN)_6$$

$$2Ni^{++} + Fe(CN)_6^{----} = Ni_2Fe(CN)_6$$

$$2Co^{++} + Fe(CN)_6^{----} = Co_2Fe(CN)_6$$

(3) Also the potentiometric titrations were compared with potassium and sodium ferrocyanides by ferric chloride and silver nitrate solution at the same condition or different conditions, and a very good agreement was found with each other.

(4) In this titration we found that the reaction takes place as reported already by Niemz[1] at the case of silver and in other case as follows:

$$4Ag^{+} + Fe(CN)_6^{----} = Ag_4Fe(CN)_6$$

$$4Fe^{+++} + 3Fe(CN)_6^{----} = Fe_4[Fe(CN)_6]_3.$$

Yokohama Higher Technical School, Yokohama.

(1) Niemz, Dissert. Dresden (1920).

DISPERSITY OF CATALYST AND CATALYTIC ACTIVITY.

By Kiyoshi YOSHIKAWA.

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A most simple case of mixed catalysts is that in which a mixture of two substances, the one catalytically active and the other inert, forms a catalyst. In hydrogenation catalysis, a catalyst composed of nickel with an irreducible oxide such as kieselguhr, alumina, magnesia, etc. may be cited as an example. The name promoters may be given to these oxides, when the addition of a small quantity of them greatly increases the catalytic activity of nickel. The oxides may be termed carriers or supports, when nickel is distributed on a large quantity of them, the activity being not materially enhanced. It is evident, however, that to class these oxides either as promoters or as carriers is not always possible, because no decisive line of demarcation can be drawn between them. The author has studied the hydrogenation of acetylene using the nickel-kieselguhr and palladium-kieselguhr catalysts. Attention has been devoted to the modification of the catalytic activity produced by admixture with inert substance. The quantity of kieselguhr added to the catalytic agent has considerable influence on the activity of the resulting catalyst. In the presence of nickel alone and with excess of hydrogen, acetylene is hydrogenated completely to ethane. By passage over nickel or palladium distributed on a suitable amount of kieselguhr, acetylene is hydrogenated exclusively to ethylene. The composition of the products depends on the relative proportion of nickel and kieselguhr or palladium and kieselguhr. These results suggest a possible mechanism of one case of promoter and carrier actions and on the other hand, a method of selective hydrogenation of acetylene to ethylene.

(1) A Possible Mechanism of One Case of Promoter and Carrier Actions. The phenomenon which is met with, namely the markedly selective action of catalysts produced by varying the dispersity of the catalytic agent on an inert substance, can not be explained from the standpoint of the problem of the quantity of a catalytic agent. This can hardly be due simply to the diminution in the amount of a catalyst, since the prolonged contact with a catalyst can not cause the production of ethane. In order to offer the explanation, the author assumes the co-activation of neighbouring active centres on the catalytic surface

by the heat of reaction. A surface of catalyst may present centres of various degrees of activeness. At the start of a catalytic reaction, the centre of maximum activity, the point A, on the surface is activated and the reaction takes place at first on the point A. The reaction is exothermic and the heat of reaction may excite the neighbouring active point B and the reaction occurs on the point B. The heat of the reaction may excite not only the new active point C but also the original active point A, which is further stimulated. Thus the co-activation of active centres is achieved and the proportion of stimulated active points increased and the reaction correspondingly accerelated. After the attainment of equilibrium between accumulation and loss of heat, the reaction proceeds with constant velocity. Now the case may be considered in which a catalytically active substance is spread on a relatively large amount of non-catalytic material. If the dispersity of the catalytic agent is sufficiently large, the distance between the neighbouring active points on the surface may be long enough to disable the efficient co-activation, so that the catalytic centres can not display their full activities. There may be cases where the hydrogenation of acetylene to ethylene is possible but the hydrogenation to ethane is impossible. In most cases carriers are employed on purpose to increase the surface area of catalysts and to gain the superior activity. In this work the extreme case has been discussed in which the extent of distribution of catalytic metal on carriers is so great that the restriction of the activity can be observed. At the other extreme, the case in which a metal catalyst is admixed with a minute amount of inert oxides, may be considered. In such a case, the distance between the active points is nearly the same as that on the pure metal. The presence of an inert oxides, which is a bad conductor of heat, interspersed among the active centres, favours the accumulation of the reaction heat. The effect is the equivalent of an extremely high local temperature. Therefore, the co-activation of active centres being enhanced, the reaction velocity is greatly increased. The cases in which a metallic catalyst is stimulated by the presence of traces of irreducible oxides are very numerous and in the case where the reaction is a simple addition of hydrogen, the primary function of the promoter action may be regarded as the enhanced co-activation of active centres by the heat of reaction.

The author arrives at the conclusion with regard to the modification of a straight hydrogenation process—the simple addition of hydrogen at an unsaturated linkage—in presence of a metallic catalyst, an inert irreducible oxide such as kieselguhr, alumina, magnesia, etc. being em-

ployed as the promoter and as the carrier, that the stimulation and the restriction of catalytic activity can be satisfactorily explained on the basis of enhanced and unfavoured co-activation of active centres by the heat of reaction.

(2) Hydrogenation of Acetylene to Ethylene. In a series of investigations of von Wilde[1], Sabatier[2], and more recently Morris[3] it was shown that acetylene was easily hydrogenated to ethane, ethylene and liquid products in presence of metallic catalysts. Paal[4] and Ross[5] have investigated the hydrogenation to get ethylene and they were able to obtain the product containing 80% ethylene, the former employing colloidal palladium shaken with water, the latter in presence of nickel catalyst. Much attention has been given to the problem of preparing ethylene by the hydrogenation of acetylene, and several patents have been claimed for the technical hydrogenation. The author observed that acetylene was readily hydrogenated to ethylene by the employment of the palladium catalysts distributed on the proper amount of kieselguhr (500-1500 parts of kieselguhr added to one part of palladium). With equal volumes of acetylene and hydrogen the product contains 90% ethylene and 2-3% saturated hydrocarbons.

Experimental.

Acetylene was prepared by the action of water on calcium carbide. The removal of the impurities was accomplished by the method described in Vanino's "Präparativen Chemie." For the experiments with nickel catalysts, acetylene was solidified with liquid air and subjected to a fractional distillation. To poisons, nickel is more sensitive than palladium and without this treatment no satisfactory results were obtained. Hydrogen was obtained from cylinder of commercial electrolytic hydrogen and no attempt was made to remove the impurities except to bubble the gas through potassium hydroxide solution.

Nickel-kieselguhr catalyst was prepared by the reduction of nickel oxide admixed with kieselguhr, which was obtained by the calcination of the mixture of nickel nitrate and kieselguhr. Palladium-kieselguhr catalyst was prepared from palladium chloride solution, into which

(1) von Wilde, *Ber.*, **7** (1874), 352.
(2) Sabatier et Senderens, *Compt. rend.*, **128** (1899), 1173; **130** (1900), 1559.
(3) Morris and Reyerson, *J. Phys. Chem.*, **31** (1927), 1332.
(4) Paal und Hoheneggen, *Ber.*, **48** (1915), 275.
(5) Ross, Culbertson and Parsons, *J. Ind. Eng. Chem.*, **13** (1921), 775.

kieselguhr was added, by reduction to metal with formaldehyde.[1] The solution was heated on water-bath until the precipitation of palladium was completed and then filtered. For palladium catalysts, commercial kieselguhr was used with no further purification and for nickel catalysts kieselguhr was purified by boiling with hydrochloric acid solution.

The experiments were carried out by the flow method. The apparatus used is represented in Fig. 1. A mixture of acetylene and

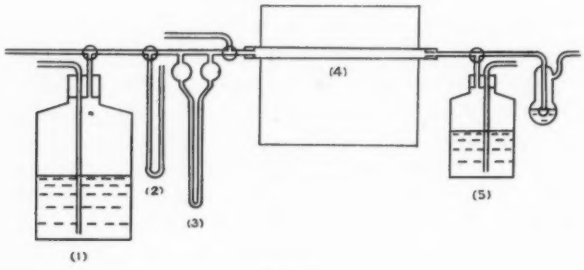

Fig. 1.

hydrogen stored in the reservoir (1) was introduced through the manometer (2) and the flowmeter (3) into the catalyst tube (4) placed in a gas furnace. The tube was made of glass, 46 cm. long and 1.4 cm. in diameter. The temperature was indicated by the thermometer placed outside the tube. The reaction products were collected into the reservoir (5). The reservoirs (1) and (5) were three litre and one litre bottles respectively and saturated sodium chloride solution was used as a confining liquid. A U-glass tube, 1.5 cm. in diameter, was occasionally used as a catalyst tube for the experiments run at the temperatures below 130°C. The tube was filled with the catalyst supported on granules of quartz and immersed in a glycerin-bath. In carrying out the hydrogenation, the catalyst tube was heated to the desired temperature, hydrogen being streamed into the tube. And the mixture of acetylene and hydrogen in the reservoir (1) was passed over the catalyst. When about one litre of the gases was passed, it was felt that the system had reached a steady state. Then the product was collected into the reservoir (5) and the extend of hydrogenation was determined by the analysis of the product.

(1) Willstätter und Waldschmidt-Leitz, *Ber.*, **54** (1921), 123.

Analyses of acetylene and ethylene were carried out according to the method of Treadwell[1] modified by Fujio[2]. Acetylene, ethylene and heavy hydrocarbons were determined by the absorption with the solution of mercuric cyanide, mercuric nitrate and fuming sulphuric acid respectively. After the removal of the above gases, hydrogen and saturated hydrocarbons were estimated by oxidation with cupper oxide at 300°C. and 600°C. The saturated hydrocarbons consisted of ethane and methane.

(1) Experiments on the Effects of Dispersity of Catalysts. Mixtures of one volume of acetylene and nearly two volumes of hydrogen were passed over nickel-kieselguhr catalysts at the rate of flow 5 litres per hour. Mixtures of nearly equal volumes of acetylene and hydrogen were passed over palladium-kieselguhr catalysts at the rate of flow 7 litres per hour. The composition of the resulting gases greatly depends on the dispersity of catalysts on kieselguhr. In the presence of the catalysts of small dispersity, the hydrogenation proceeds to ethane and the production of ethylene decreases. Table 1 gives the results of the experiments.

Excess of hydrogen in the reacting gases favours the production of ethane and the tendency is remarkable in presence of the catalysts of small dispersity. Table 2 gives the results of the experiments.

(2) Experiments on the Production of Ethylene. The effects of variation in the composition of reacting gases, reaction temperature, the rate of flow, and the addition of steam to the gases in the hydrogenation, were observed in presence of palladium-kieselguhr catalysts. From the estimation of the volumes and the composition of the gases before and after the hydrogenation, the yields of the products were calculated. Tables 3 and 4 give the results. Table 5 gives the results of the experiments with palladium distributed on the purified kieselguhr and anhydrous silicic acid.

Author's thanks are due to Prof. Dr. Bennosuke Kubota for his helpful advice and his kindly interest in the progress of this research.

(1) Treadwell und Tauber, *Helv. Chim. Acta*, **2** (1919), 601.
(2) Fujio and Shirai, *Kaigun Nenryôshô Jikkenhôkoku* (*Experimental Reports of the Japanese Naval Institute of Fuel.*), **4**, No. 4, 47.

Table 1.

Nickel-kieselguhr Catalysts

Parts of kieselguhr added to one part of nickel	Reaction temperature	C_2H_2	C_2H_4	Heavy hydrocarbons	H_2*	CH_4	C_2H_6	N_2
0	100°	.0	.0	.9	34.8	57.9		6.4
20	100°	.0	5.1	1.1	43.9	41.5		8.4
100	100°	.0	15.8	.6	63.5	2.8	6.8	11.3
200	150°	.4	16.8	1.2	64.8	3.6	.8	12.2
500	200°	.9	12.6	1.1	70.8	2.8	.0	13.8

* Hydrogen was found in abundance, because acetylene underwent the polymerisation into liquid hydrocarbons.

Palladium-kieselguhr Catalysts

Parts of kieselguhr added to one part of palladium	Reaction temperature	C_2H_2	C_2H_4	Heavy hydrocarbons	H_2	C_2H_6	N_2
50	110°	3.8	67.3	.9	1.3	22.5	4.1
150	120°	2.7	79.5	.7	1.4	9.1	6.1
500	120°	1.2	91.3	.4	1.2	2.4	4.4
800	180°	2.2	88.4	.3	.2	1.7	7.1
1500	170°	2.3	90.2	.5	1.3	1.8	4.1

Palladium-kieselguhr Catalysts

Parts of kieselguhr added to one part of palladium	Reaction temperature	C_2H_2	C_2H_4	Heavy hydrocarbons	H_2	C_2H_6	N_2	
500	150°	1.8	90.7	.5	.0	2.6	4.4	Excess of acetylene
500	180°	2.2	91.4	.5	.0	1.1	4.8	Excess of acetylene
500	150°	1.0	83.2	.8	2.3	7.2	5.4	Excess of hydrogen
1500	200°	2.4	90.8	.2	.3	1.5	4.8	Excess of acetylene
1500	200°	1.3	84.7	.3	6.6	2.5	4.6	Excess of hydrogen
1500	150°	2.4	86.3	.8	3.1	2.6	4.8	Excess of hydrogen

Table 2.

Palladium-kieselguhr Catalysts (500 parts of kieselguhr added to one part of palladium)

Reaction temperature	Rate of flow l./hr.		Volumes c.c.	C_2H_2	C_2H_4	Heavy hydrocarbon	H_2	C_2H_6	N_2	Others*	
170°	6.0	Original	1600	47.8	—	—	49.4	—	2.7		
		Product	680	1.1	89.1	.3	.0	4.4	5.1		
	% of C_2H_2 converted to			1.0	79.3	—	—	3.9	—	15.8	
170°	6.0	Original	1800	50.5	—	—	47.3	—	2.2		
		Product	770	3.3	90.7	.4	.0	1.7	3.9		
	% of C_2H_2 converted to			2.8	76.8	—	—	1.4	—	19.0	
180°	6.5	Original	1700	39.2	—	—	57.8	—	3.0		Excess of hydrogen
		Product	810	2.3	50.1	1.2	27.1	11.5	5.6		
	% of C_2H_2 converted to			2.8	61.0	—	—	14.0	—	22.2	
170°	6.0	Original	1300	48.5	—	—	48.9	—	2.4		Addition of steam
		Product	570	2.4	90.4	.4	.0	1.6	5.4		
	% of C_2H_2 converted to			2.2	81.0	—	—	1.4	—	14.8	
185°	6.5	Original	1700	49.1	—	—	48.3	—	2.6		Addition of steam
		Product	710	.8	90.3	.4	1.9	2.7	4.9		
	% of C_2H_2 converted to			.7	76.7	—	—	2.3	—	20.3	
185°	6.0	Original	1700	49.6	—	—	48.3	—	2.1		
		Product	680	2.3	88.0	.5	1.6	2.1	5.4		
	% of C_2H_2 converted to			1.9	71.1	—	—	1.7	—	25.3	
180°	13.0	Original	1800	47.7	—	—	50.7	—	2.4		
		Product	750	2.7	80.5	.8	8.7	2.7	4.6		
	% of C_2H_2 converted to			2.4	70.3	—	—	2.4	—	24.9	
150°	7.0	Original	1600	38.5	—	—	59.2	—	2.3		Excess of hydrogen
		Product	630	2.7	53.3	.8	32.7	5.5	4.9		
	% of C_2H_2 converted to			3.6	70.1	—	—	7.2	—	19.1	
185°	6.0	Original	1700	50.1	—	—	47.9	—	2.0		Addition of steam
		Product	680	2.1	88.8	.7	1.7	1.7	5.0		
	% of C_2H_2 converted to			1.7	71.0	—	—	1.4	—	25.9	

Table 2.—(*Concluded*)

Reaction temperature	Rate of flow l./hr.		Volumes c.c.	C_2H_2	C_2H_2	Heavy hydrocarbons	H_2	C_2H_6	N_2	Others	
130°	7.2	Original	1800	48.0	—	—	49.9	—	2.1		U-glass tube used as catalyst tube
		Product	720	2.3	86.8	.4	.8	3.5	6.2		
	% of C_2H_2 converted to			1.9	72.3	—	—	2.9	—	22.9	
135°	12.3	Original	1800	49.7	—	—	47.6	—	2.7		U-glass tube used as catalyst tube
		Product	760	4.1	83.7	.6	5.5	1.6	4.4		
	% of C_2H_2 converted to			3.5	71·0	—	—	1.4	—	24.1	
100°	3.7	Original	1500	50.3	—	—	47.5	—	2.2		U-glass tube used as catalyst tube
		Product	600	4.6	81.5	1.0	4.7	3.2	4.9		
	% of C_2H_2 converted to			3.7	65.8	—	—	2.6	—	27.9	
110°	3.9	Original	1800	47.6	—	—	49.2	—	3.2		
		Product	760	3.3	81.1	1.2	.6	6.0	7.8		
	% of C_2H_2 converted to			2.9	71.8	—	—	5.3	—	20.0	

* Hydrogenation was accompanied by the polymerisation of acetylene to liquid hydrocarbons. The figures were determined by difference.

Table 3.

Palladium-kieselguhr Catalysts (1500 parts of kieselguhr added to one part of palladium)

Reaction temperature	Rate of flow l./hr.		Volumes c.c.	C_2H_2	C_2H_4	Heavy hydrocarbons	H_2	C_2H_6	N_2	Others	
190°	6.5	Original	1800	45.7	—	—	50.2	—	4.1		
		Product	800	2.9	78.3	.5	8.8	2.7	6.7		
	% of C_2H_2 converted to			2.8	76.1	—	—	2.6	—	18.5	
200°	7.0	Original	1400	37.5	—	—	60.4	—	2.1		Excess of hydrogen
		Product	780	1.4	49.1	.7	42.4	2.1	4.3		
	% of C_2H_2 converted to			2.1	73.0	—	—	3.1	—	21.8	

Table 3.—(*Concluded*)

Reaction temperature	Rate of flow l./hr.		Volumes c.c.	C_2H_2	C_2H_4	Heavy hydrocarbons	N_2	C_2H_6	H_2	Others	
200°	9.3	Original	1700	38.0	—	—	60.0	—	2.0		Excess of hydrogen
		Product	940	1.8	52.5	.8	38.2	2.2	4.5		
	% of C_2H_2 converted to			2.6	76.4	—	—	3.2	—	17.8	
200°	11.5	Original	1 00	37.9	—	—	59.1	—	3.0		Excess of hydrogen
		Product	880	2.1	55.5	.8	32.0	3.9	5.7		
	% of C_2H_2 converted to			3.0	80.5	—	—	5.7	—	10.8	
200°	6.0	Original	1700	50.2	—	—	47.5	—	2.2		Addition of steam
		Product	700	2.2	86.9	.5	3.4	1.7	5.1		
	% of C_2H_2 converted to			1.8	71.2	—	—	1.4	—	25.6	
190°	5.5	Original	1700	49.0	—	—	47.9	—	2.1		Addition of steam
		Product	690	3.0	85.7	.9	4.3	1.6	4.5		
	% of C_2H_2 converted to			2.5	71.0	—	—	1.3	—	25.2	

Table 4.

Palladium-kieselguhr Catalysts (500 parts of purified kieselguhr added to one part of palladium)

Reaction temperature	Rate of flow l./hr.		Volumes c.c.	C_2H_2	C_2H_4	Heavy hydrocarbons	H_2	C_2H_6	N_2	Others
170°	7.0	Original	1800	49.3	—	—	48.8	—	1.9	
		Product	800	5.9	83.4	.7	3.6	2.7	4.6	
	% of C_2H_2 converted to			5.3	75.1	—	—	2.4	—	17.2
150°	5.0	Original	1700	49.0	—	—	48.0	—	2.0	
		Product	730	2.3	87.8	.7	1.3	3.7	5.3	
	% of C_2H_2 converted to			2.0	76.8	—	—	3.2	—	18.0
170°	6.2	Original	1700	37.1	—	—	59.9	—	3.0	
		Product	900	2.0	47.2	1.3	30.3	12.7	6.5	
	% of C_2H_2 converted to			2.9	67.3	—	—	18.1	—	21.7

Table 5.

Palladium-anhydrous silicic acid Catalysts (500 parts of anhydrous silicic acid added to one part of palladium)

Reaction temperature	Rate of flow l./hr.		Volumes c.c.	C_2H_2	C_2H_4	Heavy hydrocarbons	H_2	C_2H_6	N_2	Others
150°	4.8	Original	1800	49.9	—	—	47.9	—	2.2	
		Product	740	4.0	88.1	.6	.0	4.2	3.1	
	% of C_2H_2 converted to			3.3	72.6	—	—	3.4	—	20.7
170°	9.0	Original	1800	49.2	—	—	48.7	—	2.1	
		Product	750	2.6	88.3	.8	.2	3.6	4.5	
	% of C_2H_2 converted to			2.2	74.8	—	—	3.1	—	19.9

Summary.

1. In the study of the hydrogenation of acetylene in presence of nickel and palladium catalysts distributed on kieselguhr, it was observed that markedly selective action of catalysts was produced by the variation of the dispersity of the catalytic agents on kieselguhr. The phenomenon which was met with, suggests a possible mechanism of one case of promoter and carrier actions and on the other hand, a method of hydrogenation of acetylene to ethylene.

2. With regard to the simple hydrogenation process, in presence of a metallic catalyst, inert irreducible oxides being employed as the promoter and as the carrier, stimulation and restriction of the catalytic activity can be explained on the basis of the assumed co-activation of active centres on the catalytic surface by the heat of reaction.

3. Acetylene was readily hydrogenated to ethylene by the employment of the palladium-kieselguhr catalysts of proper dispersity. With equal volumes of acetylene and hydrogen, the product containing more than 90 per cent. ethylene, was obtained.

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SYNTHESIS OF *d*-TALOSE FROM *d*-GALACTOSE.

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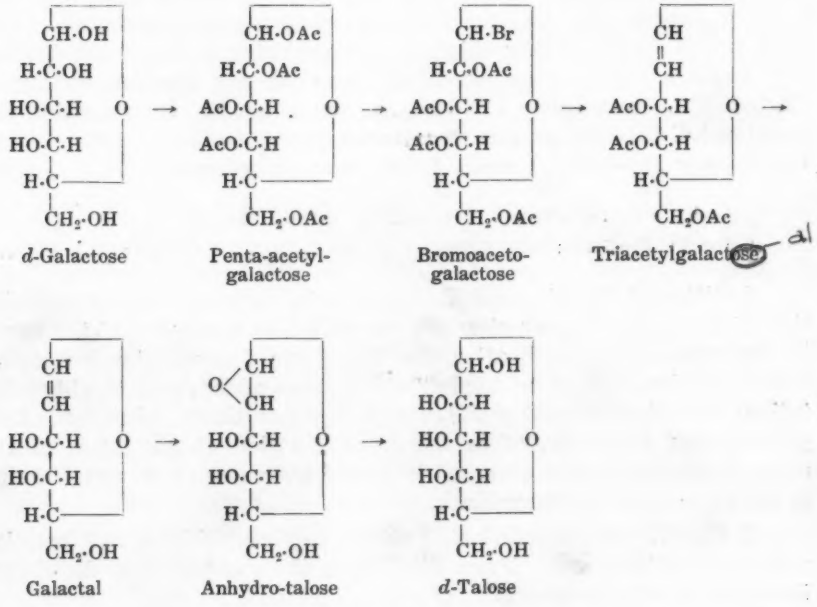
Whilst the research reported in this paper was in progress, Levene and his collaborator[1] published the results of an investigation of the same subject. Accordingly, the results already obtained, though somewhat imperfect, are published in their present form.

It has been shown by Bergmann and Schotte[2] that *d*-glucose is converted into *d*-mannose by the action of perbenzoic acid on the glucal derived from the former. By a similar method, the present author prepared *d*-talose from *d*-galactose through galactal as shown in the following scheme:



(1) *J. Biol. Chem.*, **93** (1931), 631.
(2) *Ber.*, **54** (1921), 440.

Experimental.

Preparation of Penta-acetylgalactose and its Conversion into Acetobromogalactose.

Penta-acetylgalactose was first prepared by Erwig and König's method[1] by heating *d*-galactose with freshly distilled acetic anhydride and fused sodium acetate, and the acetate was then by Fischer and Armstrong's method[2] converted into acetobromogalactose by the action of hydrogen bromide in glacial acetic acid on it.

Preparation of Triacetylgalactal. Thirty grams of acetobromogalactose were mixed with 60 gr. of zinc dust and 300 c.c. of cold 50 per cent. aqueous acetic acid. The mixture was shaken for one hour and a half, and the zinc dust was filtered off. The colourless filtrate was diluted with water, and extracted several times with ether. The ethereal solution was washed with water, neutralised with a solution of sodium bicarbonate, and again washed with water. After being dried over anhydrous sodium sulphate, the ethereal solution was evaporated. The faint yellow viscid oil thus obtained was subjected to fractional distillation under a high vacuum of 0.3–0.4 mm., when a fraction boiling at 128.5–154°C. (principally 149–154°C.) was collected. On repeating the fractional distillation, an almost colourless syrup boiling at 128.5–140°C. (principally 138–140°C.) under 0.2–0.3 mm. passed over:

Anal.: Subst. = 3.125 mg. CO_2 = 6.107; H_2O = 1.740 mg.
Found: C = 53.30; H = 6.23 %. Calc. for $C_{12}H_{16}O_7$: C = 52.94; H = 5.88 %.

Addition of Bromine and Hydrogen. An excess of chloroform solution of bromine of known strength was added to a solution of the syrup in the same solvent and, after standing for a few minutes, potassium iodide solution and dilute sulphuric acid were added, and the liberated iodine was titrated with a N/10-sodium thiosulphate solution: 0.1120 gr. absorbed 0.0695 gr. of bromine. A solution of one gram of the syrup in absolute ether absorbed 90 c.c. of hydrogen at 0° and 760 mm. in the presence of platinum black.

$C_{12}H_{16}O_7$, with an ethylenic linking, requires 0.0660 gr. of bromine and 82 c.c. of hydrogen. From these facts, there can be little doubt that the syrup is triacetylgalactal.

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(1) *Ber.*, **22** (1889), 2207.
(2) *Ber.*, **35** (1902), 837.

Preparation of Galactal from Triacetylgalactal. From the analogy of glucose, the use of methyl alcoholic ammonia appears to be a suitable method of hydrolysing the acetylgalactal, because triacetylglucal is readily hydrolysed by the same reagent. As, however, the yield was unsatisfactory, the present author resorted to Zemplén's method.

A solution of triacetylgalactal (5 gr.) in chloroform (12.5 c.c.) was mixed with a solution of sodium (0.25 gr.) in absolute methyl alcohol (12.5 c.c.) at about –20°C., and the additive compound was hydrolysed by ice-cold water to ethyl acetate and galactal. After being neutralised with dilute hydrochloric acid, the aqueous layer was separated from the chloroform layer, shaken with animal charcoal, and filtered. The filtrate was evaporated to complete dryness under diminished pressure, when a colourless syrup was obtained. This syrup was freed from sodium chloride by dissolving it in cold absolute alcohol and filtering off any insoluble matter. In order to remove the last traces of sodium chloride, the operation was repeated several times. The syrup thus purified was still further purified by repeatedly dissolving it in cold absolute alcohol and precipitating it with absolute ether, when colourless needles were obtained in an almost quantitative yield, which melted at 95–100°C. with somewhat decomposition. The galactal thus obtained was to some extent hygroscopic, and still contained the traces of ash, which were very difficult to remove by recrystallisation. It readily decolorises bromine in a chloroform solution. For the next preparation, it was used without further purification.

Preparation of *d*-Talose from Galactal. For this purpose, perbenzoic acid was first prepared by a slight modification of Hibbert and Burt's method,[1] namely by carrying out each stage of reactions as rapidly as possible.[2] To a solution of 10 gr. of galactal in 120 c.c. of water, a solution of perbenzoic acid (12.6 gr.) in chloroform (70 c.c.) was added, and the mixture was cooled to about 0°C., stirred vigorously for an hour and left overnight in ice-cold water. The aqueous layer was separated from the chloroform layer, washed several times with ethyl acetate, and evaporated to a small bulk under diminished pressure.

An aliquot portion was treated with an excess of phenylhydrazine and warmed on a water-bath, when yellow crystals, melting at 184–185°C., were obtained, which were identified as galactosazone by the mixed melting point method.

(1) *J. Amer. Chem. Soc.*, **47** (1925), 2240.

(2) When a chloroform solution of perbenzoic acid was kept in a dark place without being previously dried, no appreciable change was observed in the concentration, even after standing for one month and a half.

The remainder was evaporated to a syrupy consistency and a solution of 1.3 gr. of the syrup in 0.5 c.c. of water was then mixed with 0.78 gr. of phenylhydrazine. After standing for three hours, the pale yellow crystals were collected, washed with ether, and purified by dissolving them in absolute alcohol, and precipitating them with absolute ether. After being washed with ether, and dried over a vacuum desiccator, they melted with decomposition at 150–178°C. As the melting points of talose and galactose phenylhydrazones are 178°C. and 160–161°C., respectively, the product consisted presumably of a mixture of *d*-talose and *d*-galactose phenylhydrazones.

Preparation of the α-Methylphenylhydrazone. A solution of the syrup (1 gr.) in water (5 c.c.) was mixed with an absolute alcoholic solution of α-methylphenylhyrazine (0.9 gr.) and the mixture was warmed on a water-bath for a short time, when colourless needles were obtained, which were collected after standing for three hours. After being successfully washed with alcohol and with ether, the crystals (m.p. 160–164°C.) were recrystallised from 30 per cent. methyl alcohol, from which they separated in colourless crystals, melting at 181.5–182°C. A mixed melting point determination with an authentic galactose-α-methylphenylhydrazone (m.p. 189–190°C.) gave m.p. 176–177°C.

From these facts, it appears that the syrup consisted of galactose and talose.

For the isolation of talose, the syrup was treated as follows: Five grams of the syrup were dissolved in water (25 c.c.) and an absolute alcoholic solution of the calculated quantity of α-methylphenylhydrazine was mixed. The mixture was allowed to stand overnight in the dark, when colourless needles of α-methylphenylhydrazone separated, which were collected, washed with absolute alcohol, and dried in a vacuum desiccator. The crystals (I) have a melting point of 165–166°C. This was recrystallised from 30 per cent. methyl alcohol, from which it separated in the crystals (II) melting at 177–178°C. Crystals (II) were again recrystallised from 30 per cent. methyl alcohol, from which they separated in colourless crystals (III) melting at 181–181.5°C. The yield was 2 gr. The mother liquor from crystals (I) was concentrated to a small bulk on a water-bath, when the crystals (IV) separated, which, after being diluted with water, were collected. The crystals were washed with the least possible quantity of absolute alcohol and ether, and then dried in a vacuum, when they melted at 152–153°C. The crystals were recrystallised twice from 30 per cent. methyl alcohol, from which they separated in the crystals (V) melting at 153–153.5°C.

Talose-α-methylphenylhydrazone was thus separated from galactose-α-methylphenylhydrazone by taking advantage of the great solubility of the former in methyl alcohol.

Crystals (III) and (V) were analysed with the following results:—

(1) Analysis of Crystals (III): 3.029 Mg. of the air-dried substance lost 0.123 mg. on heating at 105–106°C. under diminished pressure. Found: $H_2O = 4.07\%$. Calc. for $C_{13}H_{20}O_5N_2$, H_2O: $H_2O = 5.96\%$.

Anhydrous substance = 2.906; $CO_2 = 5.809$; $H_2O = 1.693$ mg. And subst. = 3.830 mg.; $N_2 = 0.321$ c.c. at 14.5°C. and 761.7 mm. Found: C = 54.52; H = 6.52; N = 9.97%. Calc. for $C_{13}H_{20}O_5N_2$: C = 54.90; H = 7.04; N = 9.86%.

(2) Analysis of Crystals (V): This substance contained no water of crystallisation. Subst. = 3.235; $CO_2 = 6.516$; $H_2O = 2.075$ mg. And subst. = 3.320 mg.; $N_2 = 0.276$ c.c. at 15°C. and 761.8 mm. Found: C = 54.93; H = 7.01; N = 9.88%. Calc. for $C_{13}H_{20}O_5N_2$: C = 54.90; H = 7.04; N = 9.86%.

Decomposition of the α-Methylphenylhydrazone (m.p. 181–181.5°C.) **with Benzaldehyde.** The α-methylphenylhydrazone (0.5 gr.) was mixed with a solution of benzaldehyde (0.6 gr.) in 50 per cent. alcohol (11 c.c.) and the mixture was heated on a water-bath for about two hours, when an oily product separated, which, on cooling, solidified to a pale yellow mass. After being allowed to stand overnight, it was collected, washed with alcohol and dried. The crystals thus obtained melted at 104–105°C., and this melting point was not altered on admixture with an authentic specimen of benzaldehyde-α-methylphenylhydrazone. The filtrate from the benzaldehyde-α-methylphenylhydrazone was diluted with water and most of the alcohol was removed by evaporation. After being extracted with ether, the aqueous residue was evaporated and dissolved in hot alcohol, which, on cooling, separated as colourless crystals. This was washed with 80 per cent. alcohol, when it melted at 164–165.5°C. and produced no depression of the melting point on admixture with an authentic specimen of *d*-galactose. Its specific rotation was $[\alpha]_D^{19} = +78.8°$ (in water).

The Decomposion of the α-Methylphenylhydrazone (m.p. 153–153.5°C.) **with Benzaldehyde.** The decomposition of the α-methylphenylhydrazone (0.3 gr.) with a solution of benzaldehyde (0.6 gr.) in alcohol (6 c.c.) and the treatment of the filtrate from benzaldehyde-α-methylphenylhydrazone were carried out similarly as in the case of the above fraction. The aqueous solution was evaporated to a small bulk, decolorised with animal charcoal, and again evaporated to dryness, when a colourless mass was obtained, which was recrystallised from water. The specific rotation of the crystals in water was $[\alpha]_D^{17} = +14.8°$.

Owing to the lack of the available substance, no determination of the melting point was made with certainty.

In conclusion, the author wishes to express his hearty thanks to Professor Hiroshi Nomura, under whose guidance this investigation was carried out.

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NONEXISTENCE OF THE TWO MODIFICATIONS IN LIQUID NITROBENZENE AND CARBON BISULPHIDE.

By Eiji MURAKAMI.

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It has often been reported that some of the polar liquids undergo a sudden change in their dielectric constant in the neighbourhood of freezing point. Recently, M. Wolfke and J. Mazur, considering that it might be due to some polymorphic transformation of the liquid state and that consequently any change of other physical properties would exist, studied heating curves, dielectric constants and densities of ethyl ether, nitrobenzene and carbon bisulphide.(1) They concluded that a "modification change of liquid" exists at the following temperature.

Ethyl ether, −105°C.
Nitrobenzene, 9.5°C.
Carbon bisulphide, −90°C.

This year, Massy, Warren and Wolfenden(2) have measured the density and viscosity of nitrobenzene and concluded, contrary to the opinion of Wolfke and Mazur, that there is not two modifications in liquid nitrobenzene.

Nitrobenzene.

Material. One kilogram of pure nitrobenzene from Kahlbaum ("aus kryst. Benzol") was dehydrated over calcium chloride and distilled. The part distilled at 206°C. was collected and then subjected to fractional crystallisation. The portion (100 c.c.) of highest melting point was redistilled twice under reduced pressure. The melting point of the

(1) Mazur, *Nature*, **126** (1930), 649 & 993; **127** (1931), 270 & 893; **128** (1931), 673 & 761. Wolfke and Mazur, ibid., **126** (1930), 684; **127** (1931), 236, 741 & 926; **128** (1931), 584.
(2) Massy, Warren and Wolfenden, *J. Chem. Soc.*, **1932**, 91.

sample thus obtained was 5.67°C. The melting point of nitrobenzene obtained by various authors are as follows.

5.7°	Hansen, *Z. physik. Chem.*, **48** (1904), 595.
5.82	Meyer, *Chemisches Zentralblatt*, **1909**, II, 1842.
5.70	Timmermans, ibid., **1911**, I, 1669[1],
5.67	Swarts, *Rec. trav. chim. Pays-Bas*, **33** (1914), 284.
5.75	Turner and Polland, *J. Chem. Soc.*, **105** (1914), 1 62.
8.70 (?)	Landolt-Börnstein, "Tabellen", 1923.
5.668	Roberts and Bury, *J. Chem. Soc.*, **123** (1923), 2037.
5.689	Sidgwick and Ewbank, *J. Chem. Soc.*, **125** (1924), 2269.
5.5	Mazur, *Nature*, **127** (1931), 741.
5.77	Massy, Warren and Wolfenden, *J. Chem. Soc.*, **1932**, 92.

It is certain that the sample used by Mazur was not quite pure. Wolfke and Mazur synthesised the nitrobenzene from benzene crystals[2] and found its melting point to be 5.5°C. They said that the substance was thoroughly liquid at 5.7°C.[3] Masson[4] synthesised nitrobenzene from pure benzene and acids and obtained a sample freezing at 5.83°C. and found that the freezing point descends about 0.1° when exposed to air. He pointed out that the value reported by Mazur was decidedly low.

Heating Curve. Wolfke and Mazur[5] found an arrest at 9.5°C. in the rate of temperature rise of nitrobenzene under constant heat supply. The same experiment was repeated by the present author to confirm their results. Some 20 c.c. of nitrobenzene was taken into a glass tube, provided with a thermometer and a stirrer, cooled to 7°C. and placed in a Dewar vessel. Dry air was incessantly passed to prevent the contamination by the moisture. The temperature of the liquid rised slowly. The thermometer was read every one minute. The temperature time curves thus obtained are shown in Fig. 1. Two curves in this figure have different inclinations showing the different heating rate. These curves, contrary to their results, are quite smooth and no arrest can be seen on any part of the curves.

Density. Mazur[6] found a remarkable decrease in density of nitrobenzene between 9.5° and 5.6°C., and a sharp "Knick" in the density temperature curve at 9.5°C. For the sake of convenience, the author studied the volume change with temperature of nitrobenzene by means of a dilatometer. The capacity of the dilatometer was about 7 c.c. and

(1) See Beilsteins Handbuch der organischen Chemie, 4 Aufl. Bd. 5, Erstes Ergänzungswerk, S. 124.
(2) Wolfke and Mazur, *Nature*, **126** (1930), 993.
(3) Mazur, ibid., **127** (1931), 893.
(4) Masson, ibid., **128** (1931), 726.
(5) Wolfke and Mazur, ibid., **127** (1931), 741.
(6) Mazur, ibid., **127** (1931), 893.

the diameter of its capillary was 0.6 mm. The position of menisci of the liquid at various temperatures were read. The results are plotted in Fig. 2. As seen from Fig. 2 there is no sudden change in volume, being against to the result of Mazur.

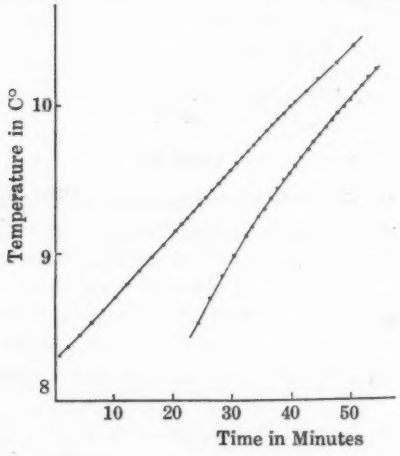

Fig. 1.

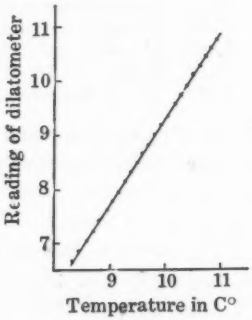

Fig. 2.

The density of nitrobenzene at 20°C. was measured by a pycnometer, and obtained the value, $d_4^{20°} = 1.2030$. The value of $d_4^{20°}$ obtained by other authors are as follows.

1.2039 Brühl, *Z. physik. Chem.*, **16** (1895), 216.
1.20328 Kahlbaum, ibid., **26** (1898), 646.
1.2028 Falk, *J. Am. Chem. Soc.*, **31** (1909), 815.
1.20323 Tyrer, *J. Chem. Soc.*, **105** (1914), 2538.

Refractive Index. Wolfke and Mazur[1] have reported, without any numerical data, that the value of the refractive index also undergoes a very distinct change at 9.6°C.

The refractive index was measured at the temperature between 7° and 20°C., especially carefully in the neighbourhood of 9.6°C., with a Pulfrich refractometer for H_α line. Owing to the construction of the refractometer it was inevitable that the sample was exposed to air, and the refractive index of nitrobenzene was found to decrease by absorbing moisture. To prevent the absorption of moisture, the liquid was protected by covering completely with rubber tubing at the upper part of the cell, as shown in Fig. 3. The vapour tension of nitrobenzene at

(1) Wolfke and Mazur, *Nature*, **128** (1931), 584.

the observation temperatures are comparatively small, so the rubber was hardly corroded, and the measurement was carried out quite satisfactorily.

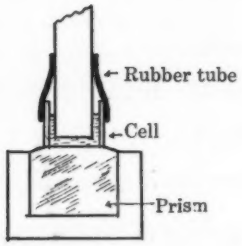

Fig. 3.

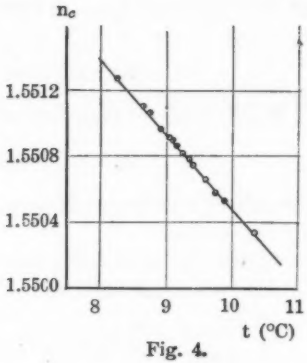

Fig. 4.

The results are given in Table 1, where n_c denotes the refractive index of nitrobenzene for H_α line. Three series of measurements have been done which indicate in Table 1 under No. 1, No. 2 and No. 3. The values of the first series are depicted in Fig. 4.

Table 1.

No. 1.		No. 2.		No 3.	
Temp. (t)	Refractive index (n_c)	Temp. (t)	Refractive index (n_c)	Temp. (t)	Refractive index (n_c)
8.25°C.	1.55127	8.40C°	1.55118	7.45°C.	1.55167
8.60	1.55114	8.55	1.55112	8.40	1.55123
8.75	1.55106	8.65	1.55105	8.65	1.55109
8.92	1.55096	8.75	1.55102	8.90	1.55099
9.05	1.55091	9.23	1.55079	9.57	1.55079
9.10	1.55089	9.45	1.55068	9.58	1.55069
9.15	1.55086	9.55	1.55063	10.00	1.55052
9.25	1.55081	9.87	1.55050	10.30	1.55038
9.35	1.55078	9.90	1.55049	10.63	1.55025
9.42	1.55075	10.30	1.55030	11.30	1.54990
9.60	1.55066	10.45	1.55025	11.85	1.54964
9.75	1.55058	10.85	1.55006	13.30	1.54899
9.90	1.55053	10.95	1.55001	14.62	1.54837
10.35	1.55034	19.88	1.54590	16.68	1.54751
				19.30	1.54625
$n_c = 1.554992 - 0.000450t$		$n_c = 1.555037 - 0.000459t$		$n_c = 1.555060 - 0.000455t$	

The relation between refractive indices and temperatures are quite linear and no sudden change is found in any part of the line. The experimental equations calculated by the method of least squares are shown in the above table. From these three equations we obtain the following one.

$$n_e = 1.555030 - 0.000455\,t.$$

Falk[1] obtained by measurement between 20° and 70°C. the relation:

$$n_e = 1.55453 - 0.000458\,t.$$

The temperature coefficient in the Falk's equation is practically identical to that of the author.

The values of refractive index for H_α line at 20°C. obtained by various authors are as follows:

1.54593 Brühl, *Z. physik. Chem.*, **16** (1895), 216.
1.54537 Falk, loc. cit. Interpolated value.
1.54582 Brand and Kranz, *J. prakt. Chem.*, **115** (1927), 153.
1.54593 Murakami.

Carbon Bisulphide.

Wolfke and Mazur[2] have reported that carbon bisulphide also exhibits the analogous phenomena as nitrobenzene in the heating curve at –90.03°C., and that the two modifications are discernible as they separate into two layers. The following experiment was carried out to ascertain this report.

Carbon bisulphide from Kahlbaum was purified with mercury and by distillation. The freezing point of the material was –111.0°C. The method of measurement of the heating curve was the same to that of nitrobenzene, excepting, in this case, the Dewer vessel containing a mixture of alcohol and ether was cooled with liquid air. When the carbon bisulphide was cooled down to −100°C., further cooling was stopped, and the rate of temperature rise was measured by means of a pentane thermometer. The result is shown in Fig. 5. As seen from this figure, the time temperature curve is nearly straight in the neighbourhood of −90°C.

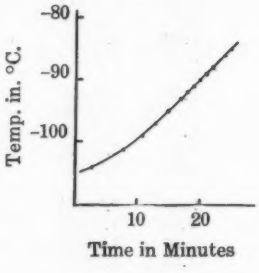

Fig. 5.

(1) Falk, loc. cit.
(2) Wolfke and Mazur, *Nature*, **127** (1931), 926.

and shows no arrest of temperature. In this case, however, as the rate of elevation of temperature is comparatively large, and the accuracy of the thermometer is not so good, the observed result may not be so accurate as the case of nitrobe zene. Moreover, two layers could not be observed anywhe e between the room temperature and the freezing point.

In conclusion the author wishes to express his hearty thanks to Professor J. Sameshima for his kind guidance throughout this experiments.

Summary.

The heating rate and the volume dilatation of nitrobenzene have been measured between 8° and 11°C. and the refractive index between 7° and 20°C. The density of nitrobenzene is $d_{20}^{4} = 1.2030$, and the refractive index for H_α line is given by the equation.

$$n_c = 1.555030 - 0.000455\, t.$$

The heating curve of carbon bisulphide has been measured between –100° and –85°C.

No arrest in the heating curves, no distinct change of the slope in the dilatation curve and no distinct change in the value of the refractive index have been observed within the range of the observed temperatures. Two layers in liquid carbon bisulphide at –90°C. could not be observed.

None of these results proves the existence of the two modifications of the liquid nitrobenzene and carbon bisulphide such as suggested by Wolfke and Mazur.

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